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(57) Abstract: An oil based drilling fluid comprising oil, a fluid loss additive and a rheology modification agent, optionally water,
optionally at least one surfactant and optionally a weighting agent characterised in that the fluid loss additive is a polymer which is
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(74) Common Representative: CIBA SPECIALTY CHEMICALS WATER TREATMENTS LIMITED; Patents Department, Cleckheaton Road, Low Moor, Bradford, West Yorkshire BD12 0JZ (GB).

(54) Title: OIL BASED DRILLING FLUID AND COPOLYMER BASED ON STYRENE, LAURYL METHACRYLATE AND (METH)ACRYLIC ACID

(57) Abstract: An oil based drilling fluid comprising oil, a fluid loss additive and a rheology modification agent, optionally water, optionally at least one surfactant and optionally a weighting agent characterised in that the fluid loss additive is a polymer which is formed from a monomer blend comprising, i) 50 to 90% by weight styrene, ii) 10 to 50% by weight C₁₀₋₂₀ alkyl (meth)acrylate iii) 0 to 10% by weight (meth)acrylic acid.

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OIL BASED DRILLING FLUID AND COPOLYMER BASED ON STYRENE, LAURYL METHACRYLATE AND (METH)ACRYLIC ACID

This invention relates to oil based drilling fluids and novel polymeric products for use therein particularly for improving the fluid loss properties.

It is standard practice to apply oil based drilling fluids during the drilling of oil wells and other bore holes in order to both lubricate the drill string and to disperse and carry cuttings away from the drill bit. It is known to use either water based or oil based drilling fluids for this purpose. Although water based drilling fluids are widely used they present certain disadvantages, which render them unsuitable in many circumstances. These disadvantages include the tendency for such water based fluids to disintegrate and disperse clay, dissolve salts and induce corrosion of iron components of equipment. In addition oil based drilling fluids offer improved lubrication, higher boiling points and lower freezing points. It is desirable that the oil based drilling mud is formulated to achieve optimum performance.

The oil based drilling fluids may comprise as the oil component hydrocarbons such as diesel, alkyl benzenes, linear alpha olefins, internal olefins, linear paraffins and the like.

An oil based drilling fluid may contain water as a discontinuous phase in an amount up to 50% by weight. An oil based fluid can be formulated without water but generally contains at least 10% water by weight. It is often preferred for the oil based drilling fluid to be formulated using 10 to 50% by weight water. In such a fluid the water would be emulsified throughout the oil continuous phase. Generally oil based drilling fluids containing dispersed water are known as invert emulsion fluids.

Often the drilling fluid also comprises a rheology modifying agent. This can be a synthetic or natural polymer that disperses and swells in the oil based fluid thus increasing its viscosity and enhancing the rheological properties. It is common practice to include certain clays in oil based drilling fluids in order to achieve the appropriate rheology for use.

It is known to include surfactants, such as emulsifiers in oil based drilling fluids. The surfactant may be used to improve the stability of the dispersed water droplets, rheology modification agent, other additives to the drilling fluid and to disperse cuttings and/or other extraneous solids that enter the drilling fluid during the drilling operation. Usually the main purpose of adding a surfactant is to stabilise the dispersed water droplets.

It is common practice to apply other additives such as weighting agents. These additives tend to be inorganic salts of high density, such as barium sulphate or other barium salts. The function of weighting agents is to increase the density of the drilling fluid in order to ensure that the drilling fluid is not displaced by aqueous fluids entering the bore hole, thus ensuring that the fluid remains in the bore hole around the drill bit and drill string.

A problem that can occur during a drilling operation is the loss of the fluid medium from the drilling fluid. This is especially problematic when drilling through rock with a high degree of porosity. In such situations the liquid phase of the drilling fluid filters through porous zones in the rock depositing the dispersed solids of the drilling fluid as a filter cake. This loss of fluid medium from a drilling fluid is generally referred to as fluid loss. Various fluid loss chemical additives have been proposed for reducing this problem. For instance it is known to use a variety of styrenic and ethylenic polymer specifically for reducing fluid loss when using oil based drilling fluids. However, all of these known fluid loss additives do not significantly reduce fluid loss without adversely affecting the rheology of the drilling fluid. Therefore it would be usual to apply fluid loss additives at a dose that will achieve some degree of fluid loss without impairing the rheology to the detriment of the drilling operation.

It would therefore be desirable to provide a fluid loss additive for an oil based drilling fluid that provides a high degree of protection against fluid loss and yet does not significantly impair the rheology of the fluid.

Thus in a first aspect of the present invention we provide an oil based drilling fluid comprising oil, a fluid loss additive, a rheology modification agent, optionally at least

one surfactant, optionally water and optionally at least one weighting agent, characterised in that the fluid loss additive is a polymer which is formed from a monomer blend comprising,

- i) 50 to 90% by weight styrene,
- ii) 10 to 50% by weight C₁₀₋₂₀ alkyl (meth)acrylate and
- iii) 0 to 10% by weight (meth)acrylic acid.

It has been found that the fluid loss properties of oil based drilling fluids are surprisingly effective when the fluid loss additive contained therein is a polymer comprising these ratios of styrene, C₁₀₋₂₀ alkyl (meth)acrylate and optionally (meth)acrylic acid. Particularly effective fluid loss properties are observed in the oil based drilling fluid when the polymer comprises 15 to 25% by weight, more preferably 19 to 21% by weight, most preferably 19 to 20% by weight C₁₀₋₂₀ alkyl (meth)acrylate. The preferred amount of styrene comprised in the polymer is 75 to 85% by weight, more preferably 79 to 81% by weight, most preferably 79 to 80% by weight. The fluid loss additive can be a polymer that also comprises 0 to 10%, preferably 0 to 5% by weight acrylic acid or methacrylic acid. Usually, however, the polymer according to this first aspect of the invention comprises 0 to about 1% (meth)acrylic acid. Preferably the polymer has an average molecular weight in the range 100,000 to 750,000, especially 150,000 to 500,000, most preferably around 200,000.

Particularly improved fluid loss is achieved when the oil based drilling fluid according to the first aspect of the invention comprises a polymer that has been formed from styrene and lauryl methacrylate and optionally acrylic acid. This improvement in fluid loss is especially when the polymer comprises the lauryl methacrylate in an amount of 19 to 21% most preferably 19 to 20% by weight, styrene in an amount of 79 to 81% by weight, most preferably 79 to 80% by weight and acrylic acid in an amount of 0 to about 1% by weight.

According to the first aspect of the invention the oil based drilling fluid comprises the polymer of styrene, C₁₀₋₂₀ alkyl (meth)acrylate and optionally (meth)acrylic acid in a

fluid loss reducing amount. Typically the amount of polymer would be the minimum amount to achieve maximum fluid loss properties. It would be possible to add more fluid loss reducing polymer than is specifically required to achieve maximum fluid loss prevention without being detrimental to the rheology of the drilling fluid. However, excess fluid loss reducing polymer would not provide any additional advantage to the fluid and thus would be wasteful.

Typically the oil based drilling fluid according to the first aspect of this invention may comprise as the fluid loss additive the polymer of styrene C₁₀₋₂₀ alkyl (meth)acrylate and optionally (meth)acrylic acid in an amount of up to 20 pounds polymer per barrel of drilling fluid (ppb) based on active polymer. Usually, however, the dose of polymer is not in excess of 10 ppb, preferably not more than 4 or 5 ppb and most preferably about 2 ppb.

It may be desired to include some water in the oil based drilling fluid in order to improve the rheological properties. For instance the drilling fluid may include 10 to 50% by weight water, preferably 20 to 30%. Where water is present in the oil based drilling fluid it preferably exists as small droplets which are uniformly dispersed throughout the oil based fluid.

It may also be desirable to add other chemical additives which enhance the rheology. For instance the oil based drilling fluid may comprise a rheology modifying agent. This can be a synthetic or natural material, for instance a clay or polymer that disperses and swells in the oil based fluid. The rheology modifying agent would normally work by increasing the viscosity and enhancing the rheological properties. When a rheology modifying agent is present it is preferably a clay which is both oil swellable and oil dispersible. Normally such a clay would be considered to be organophilic in nature or at least rendered organophilic by chemical treatment. Such clays should be easily dispersible and swellable in the oil in order to perform effectively as a rheology modification agent. Typically clay is an amine modified clay from the group of clays known as smectites, attapulgites or hectorites. The rheology modifying agent may be added in an amount of up to 5% by weight of total

composition. Preferably the amount of rheology modifying agent is 0.5 to 2% by weight, more preferably 0.5 to 1% by weight.

The oil based drilling fluid according to the first aspect of the invention may comprise a surfactant, for instance an emulsifier. The surfactant if used would be present in low concentrations but in sufficient quantities to assist in the stabilisation of the dispersed water droplets, rheology modification agent, other additives to the drilling fluid and to disperse cuttings and other extraneous solids that enter the drilling fluid during the drilling operation. Ideally the surfactant would have a low hydrophilic lipophilic balance (HLB) and should be soluble or miscible with the oil phase. The surfactant may be included in the drilling fluid in an amount up to 5% by weight of total drilling fluid, preferably 0.5 to 3%, more preferably 1 to 2%. A suitable surfactant would tend to be a chemical compound that contains a large lipophilic moiety and a relatively smaller hydrophilic moiety. Typically any commercially available surfactant which has a low HLB and is oil soluble or oil miscible could be used for this application.

It may be necessary to apply other chemical additives to the drilling fluid of the first aspect of the invention, such as weighting agents. Weighting agents tend to be inorganic salts of high density, for instance barium sulphate or other barium salts. The weighting agent may be included in an amount of up to 50 or 60% by weight of total drilling fluid, preferably 10 to 45% by weight, more preferably 25 to 40%, most preferably around 30 to 35% by weight.

In some applications the drilling fluid may be exposed to temperatures below freezing, for instance as low as -4°C or -8°C or below, and it is important in this situation the fluid loss additive remains liquid and stable such that it can still be conveniently added to the drilling fluid.

In some situations the drilling operation may encounter high temperature zones, for instance temperatures of up to at least 400°F. In such circumstance it would be important that the drilling fluid still remains sufficiently fluid. This can be particularly

problematic when the bore hole also penetrates porous formations, since the drilling fluid would be required to function with no significant impairment of the fluid loss properties.

Typically the drilling fluid according to this first aspect of the invention can be prepared by mixing together the base hydrocarbon oil, optionally water, optionally emulsifiers, optionally rheology modifiers, optionally, weighting agents and the polymer of C₁₀₋₂₀ alkyl (meth)acrylate, styrene and optionally acrylic acid polymeric fluid loss additive. The fluid would normally be rendered homogenous by a suitable homogenising equipment, such as high speed mixers or passing the fluid mixture through one or more fluid screens. Typically the mixing process may be carried out using mixing speeds of for instance up to 8,000 rpm, preferably 2,000 to 6,000 rpm. The mixing process may be as long as 20 or 30 minutes, but can be shorter times, for instance 5 or 10 or even 15 minutes.

The second aspect of the invention is directed to the use of a polymer which is formed from a monomer blend comprising,

- i) 50 to 90% by weight styrene,
- ii) 10 to 50% by weight C₁₀₋₂₀ alkyl (meth)acrylate
- iii) 0 to 10% by weight (meth)acrylic acid,

as a fluid loss additive in an oil based drilling fluid. The polymer may be provided in any convenient form by polymerisation of the monomers in the monomer blend. For instance it may be provided as a low solids solution in a suitable solvent by polymerisation of a solution of the monomer blend in said solvent. Preferably the polymer is provided as an aqueous emulsion, with the polymer present in the dispersed phase. Typically the aqueous emulsion can be prepared by well known aqueous emulsion polymerisation techniques known in the art. For instance this could be achieved by emulsifying the monomer blend into water containing a suitable emulsifier and introducing initiators in order to effect polymerisation. Preferably the polymer has an average molecular weight in the range 100,000 to 750,000, especially 150,000 to 500,000, most preferably around 200,000.

A further enhancement of the second aspect of the invention is the use of a polymer as fluid loss additive in an oil based drilling fluid, in which the polymer is in the form of a polymer in water emulsion and wherein the polymer is formed from a monomer blend comprising,

- i) 50 to 90% by weight styrene,
- ii) 10 to 50% by weight C₁₀₋₂₀ alkyl (meth)acrylate
- iii) 0 to 10% by weight (meth)acrylic acid,

In one preferred form of this second aspect of the invention the polymer in water emulsion has a pour point of below -4°C, preferably -8°C or less. Thus in this form the emulsion further comprises a pour point depressing substance, for instance glycol, diethylene glycol and the like. The pour point depressing substance if present is included in the aqueous phase of the polymer in water emulsion, in an amount of up to 15% by weight of emulsion, preferably between 5 and 10%.

In a further form of the second aspect of the invention, the polymer in water emulsion may be used in an oil based drilling fluid used at elevated temperatures, for instance up to up to 400°F. Thus in this form the performance of the fluid loss additive is maintained when drilling through high temperature subterranean environments.

Preferably the second aspect of the invention is directed to the use as a fluid loss additive in an oil based drilling fluid a polymer that has been formed from styrene and lauryl methacrylate and optionally acrylic acid. More preferably is the use of a polymer comprising lauryl methacrylate in an amount of about 19 to 21% by weight, preferably 19 to 20%, styrene in an amount of about 79 to 81% by weight, preferably 79 to 80% by weight and acrylic acid in an amount of 0 to about 1% by weight.

The third aspect of the invention is directed to a polymer which is formed from a monomer blend comprising,

- i) 75 to 85% by weight styrene,
- ii) 15 to 25% by weight lauryl methacrylate
- iii) 0 to 5% by weight (meth)acrylic acid.

Preferably the polymer is formed from a monomer blend comprising 19 to 21% by weight, most preferably 19 to 20% by weight lauryl (meth)acrylate. The preferred amount of styrene comprised in the polymer is 79 to 81% by weight, most preferably 79 to 80% by weight. The fluid loss additive can be a polymer that also comprises 0 to 5% by weight acrylic acid or methacrylic acid. Usually, however, the polymer according to this first aspect of the invention comprises 0 to about 1% (meth)acrylic acid. More preferably is the use of a polymer comprising lauryl methacrylate in an amount of 19 to 21% by weight, most preferably 19 to 20% by weight, styrene in an amount of 79 to 81% by weight, most preferably 79 to 80% by weight and acrylic acid in an amount of 0 to about 1% by weight. Preferably the polymer has an average molecular weight in the range 100,000 to 750,000, especially 150,000 to 500,000, most preferably around 200,000. The polymer can be prepared by subjecting the monomer blend to suitable polymerisation conditions selected from the group consisting of introducing thermal initiators and irradiation of the monomer

One especially preferred form of this third aspect of the invention comprises the polymer in the form of a polymer in water emulsion. Thus according to this preferred form of the invention the polymer is prepared by aqueous emulsion polymerisation. Typically the polymer in water emulsion may be prepared by any standard aqueous emulsion polymerisation technique. For instance the monomer blend would be emulsified in an aqueous continuous phase containing emulsifier and then subjected to polymerisation conditions.

In a preferable form the polymer of lauryl methacrylate, styrene with optionally acrylic acid in the form of a polymer in water emulsion is further characterised by having a pour point of below -4°C , preferably -8°C or less. In this preferred form the polymer in water emulsion further comprises a pour point depressant, for instance glycol, diethylene glycol and the like. The pour point depressant may be

present in an amount up to 15% by weight based on total weight of emulsion, preferably 5 to 15% by weight.

According to the fourth aspect of this invention a process is provided for making a polymer of styrene, lauryl methacrylate and optionally acrylic acid comprising the steps of,

- a) forming a monomer blend comprising,
 - i) 75 to 85% by weight styrene,
 - ii) 15 to 25% by weight lauryl methacrylate
 - iii) 0 to 5% by weight (meth)acrylic acid.
- b) subjecting the monomer blend of step a) to polymerisation conditions, selected from the group consisting of introducing redox initiators, introducing thermal initiators and irradiation using ultraviolet radiation.

The process may also be applied to any of the preferred embodiments of the third aspect of the invention.

The polymer according to this fourth aspect of the invention may be prepared by any known convenient means. For instance the polymer may be prepared by forming a solution for the monomer blend, comprising styrene and lauryl (meth)acrylate and optionally (meth)acrylic acid in a suitable solvent and polymerisation the monomer blend by the use of a suitable initiator system, for instance by adding redox and/or thermal initiators or irradiation using ultraviolet radiation. Preferably the polymer has an average molecular weight in the range 100,000 to 750,000, especially 150,000 to 500,000, most preferably around 200,000.

Preferably the polymer is prepared as an aqueous emulsion polymer, by emulsifying the monomer blend, comprising styrene, lauryl (meth)acrylate and acrylic acid into water which contains a suitable emulsifying agent, for instance an alkyl phenol ethoxylate. Polymerisation may be initiated by the use of suitable redox initiators, thermal initiators or radiation, such as ultraviolet radiation. Alternatively the emulsified monomer and initiator system may be added slowly to a vessel

containing water into which has been dissolved further initiator and/or emulsifier.

When the polymer is prepared by aqueous emulsion polymerisation the polymer may be present in an amount from 10 to 50%, by weight, preferably 20 to 45% by weight, most preferably 30 to 40%. The resultant polymer emulsion polymer may have an average particle size typically in the range of 80 to 150nm, preferably between 100 and 130nm, most preferably around 120nm.

Preferably the polymer of styrene, lauryl methacrylate and optionally acrylic acid is prepared by emulsifying the monomer blend into water and then subjecting it to aqueous emulsion polymerisation. Preferably the process is carried out by slowly adding the emulsified monomer to a vessel containing water. A suitable initiator system may be used to initiate the polymerisation. For instance the water held in the vessel to which the emulsified monomer is being added is may contain dissolved initiator. Preferably at least some of the initiator is added slowly to the vessel containing water simultaneously with the addition of emulsified monomer.

The following example serve to illustrate the invention.

Example 1Preparation of Polymer

A monomer emulsion is prepared by mixing 304g Styrene , 76g Lauryl Methacrylate and 3.8g Acrylic acid with 243.7g water into which has been dissolved 34.2g Ethylan HA (Nonyl Phenol 35 mole Ethoxylate) using a Silverson mixer. An initiator solution is prepared by dissolving 0.92g ammonium persulphate in 50g deionised water.

The monomer emulsion and initiator solution are added over 3 hours and 3.5 hours respectively to a 2 litre stirred reactor containing 339.6g deionised water, 3.8g Ethylan HA and 0.23g ammonium persulphate degassed with nitrogen. The temperature is maintained at 85°C throughout the addition period. The reactor contents are held for a further 1 hour at 85°C after which the contents are cooled and filtered. The resultant white emulsion polymer has a solids content of 40.0% , a pH of 3.5 and a particle size of 120nm.

Example 2Preparation of Bulk Drilling Fluid 1

The components of drilling fluid 1, shown in Table 1, are blended together using a Silverson mixer set at 6000 rpm using a square holed head.

Table 1

Components of Drilling Fluid 1	Amount
Ultidril Base Fluid ¹	818.4g
Emul HT ²	84.0g
Truvis HT ³	30.0g
Lime	72.0g
CaCl ₂ .2H ₂ O	148.7g
Water	269.7g
Barite	2328.5g

Notes

1 Ultidrill Base Fluid is a commercially available base oil

2 Emul HT is a commercially available emulsifier

3 Truvis HT is a commercially available non-polar oil viscosifier

Preparation of Bulk drilling fluid 2

The components of drilling fluid 2, shown in Table 2, are blended together using a Silverson mixer set at 6000 rpm using a square holed head.

Table 2

Components of drilling fluid 2	Amount
Low toxicity low aromatic paraffinic mineral Oil	498.52g
Kleemul ⁴	10.0g
Kleemul 50 ⁵	30.0g
Lime	24.0g
Emul Vis ⁶	8.0g
CaCl ₂ brine	474.96g
Water	217.8g
Emul Lift A ⁷	1.2g
Barite	640.6g

Notes

4 Kleemul is a commercially available emulsifier

5 Kleemul 50 is a commercially available emulsifier

6 Emul Vis is a commercially available oil rheology modification agent

7 Emul Lift is a commercially available emulsifier

Example 3**Testing of Drilling Fluid 1**

Four 350 ml aliquots of the bulk drilling fluid 1 are taken. The polymer produced in example 1 is applied to three of the aliquots at doses of 1, 2 and 4 pounds per barrel, based on the weight of active polymer. The polymer is mixed into the drilling fluid for a further 15 minutes.

The Fann rheologies of the unaged drilling fluids were measured at 120°F.

The drilling fluids are then hot rolled for 16 hours at 400°F under 250psi pressure before cooling and remeasuring the Fann rheologies at 120°F.

The HTHP (High Temperature High Pressure) fluid loss measurements are then taken at 350°F under 500psi differential pressure.

The results are shown in Table 3

Table 3

Dose of Polymer A (ppb-active)	Rheology before hot rolling				Rheology after hot rolling				HTHP Fluid loss (ml)
	PV	YP	AV	10s Gel	PV	YP	AV	10s Gel	
0	28	20	38	10	33	3	34.5	4	45
1	31	20	41	10	28	4	30	4	10
2	32	19	41.5	10	49	12	55	6	9
3	31	19	40.5	10	36	6	39	4	8
4	33	21	43.5	11	63	14	70	7	8

PV is Plastic Viscosity

YP is Yield Point

AV is Apparent Viscosity

10s Gel is a measurement of gel strength after 10 seconds.

Testing of Drilling Fluid 2

Five 350 ml aliquots of bulk drilling fluid 2 are taken. The polymer produced in example 1 is applied to four aliquots at doses of 1, 2, 3 and 4 pounds per barrel, based on the weight active polymer. The test of drilling fluid 1 is repeated for each of the aliquots of drilling fluid 2 except that the fluids are hot rolled at 250°F and the HTHP fluid loss measurements are taken at 250°F. The results are shown in Table 4.

Table 4

Dose of Polymer A (ppb-active)	Rheology before hot rolling				Rheology after hot rolling				HTHP Fluid loss (ml)
	PV	YP	AV	10s Gel	PV	YP	AV	10s Gel	
0	23	9	27.5	4	29	18	38	8	5.2
1	28	9	32.5	5	29	16	37	9	1.6
2	30	10	35	5	35	17	43.5	8	1.2
4	32	10	37	6	38	16	46	8	0.8

The results show that the inclusion of Polymer A into the drilling fluids improves fluid loss without impairing the rheological performance of the fluids to any significant extent.

Claims

1. An oil based drilling fluid comprising oil, a fluid loss additive and a rheology modification agent, optionally water, optionally at least one surfactant and optionally a weighting agent characterised in that the fluid loss additive is a polymer which is formed from a monomer blend comprising,
 - i) 50 to 90% by weight styrene,
 - ii) 10 to 50% by weight C₁₀₋₂₀ alkyl (meth)acrylate
 - iii) 0 to 10% by weight (meth)acrylic acid.
2. A drilling fluid according to claim 1 in which the polymer is formed from a monomer blend comprising,
 - i) 75 to 85% by weight styrene,
 - ii) 15 to 25% by weight C₁₀₋₂₀ alkyl (meth)acrylate
 - iii) 0 to 5% by weight (meth)acrylic acid.
3. A drilling fluid according to claim 1 or claim 2 in which the polymer is formed from a monomer blend comprising,
 - i) 79 to 81% by weight styrene,
 - ii) 19 to 21% by weight C₁₀₋₂₀ alkyl (meth)acrylate
 - iii) 0 to 1% by weight (meth)acrylic acid.
4. A drilling fluid according to any one of claims 1 to 3 in which the polymer is formed from styrene, lauryl methacrylate and optionally acrylic acid.
5. A drilling fluid according to any one of claims 1 to 4 in which the polymer is present in an amount of up to 20 pounds per barrel (ppb).
6. A drilling fluid according to any one of claims 1 to 5 in which the polymer is present in an amount of up to 5 pounds per barrel (ppb), preferably around 2 pounds per barrel.

7. A drilling fluid according to any one of claims 1 to 6 which is stable at temperatures of at least 400°F.
8. Use of a polymer as a fluid loss additive, wherein the polymer is formed from a monomer blend comprising,
- i) 50 to 90% by weight styrene,
 - ii) 10 to 50% by weight C₁₀₋₂₀ alkyl (meth)acrylate
 - iii) 0 to 10% by weight (meth)acrylic acid.
9. A use according to claim 8 in which the polymer is provided in the form of a polymer in water emulsion.
10. A use according to claim 9 in which the polymer in water emulsion has a pour point of below -4°C, preferably -8°C or less.
11. A polymer which is formed from a monomer blend comprising,
- i) 75 to 85% by weight styrene,
 - ii) 15 to 25% by weight lauryl methacrylate
 - iii) 0 to 5% by weight (meth)acrylic acid.
12. A polymer according to claim 11 which is formed from a monomer blend comprising,
- i) 79 to 81% by weight styrene,
 - ii) 19 to 21% by weight lauryl methacrylate
 - iii) 0 to 1% by weight (meth)acrylic acid.
13. A polymer according to any one of claims 11 to 12 wherein the average molecular weight is between 100,000 and 750,000.
14. A polymer according to any one of claims 11 to 13 which is in the form of a polymer in water emulsion.

15. A polymer according to claim 14 in which the emulsion has a pour point of -8°C or less.

16. A process of making a polymer of styrene, lauryl methacrylate and optionally acrylic acid comprising the steps of

a) forming a monomer blend comprising,

i) 50 to 90% by weight styrene,

ii) 10 to 50% by weight lauryl methacrylate

iii) 0 to 10% by weight (meth)acrylic acid, and

b) subjecting the monomer blend of step a) to polymerisation conditions, selected from the group consisting of introducing redox initiators, introducing thermal initiators and irradiation using ultraviolet radiation.

17. A process according to claim 16 in which the monomer blend in step a) is emulsified into water and then subjected to aqueous emulsion polymerisation.

INTERNATIONAL SEARCH REPORT

Intern: al Application No

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A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C09K7/06 E21B21/00 E21B37/06 E21B33/138 C08F212/08 C08F220/18		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C09K E21B C08F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, PAJ, WPI Data, API Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	column 8, line 45 - line 52; example 2 ---	11-15,17
X	WO 97 12010 A (NOMURA MASAKI ;SHIBA KENICHI (JP); KAO CORP (JP); ISHIKAWA YOSHINO) 3 April 1997 (1997-04-03)	16,17
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "G" document member of the same patent family		
Date of the actual completion of the international search 8 November 2000		Date of mailing of the international search report 15/11/2000
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016		Authorized officer olde Scheper, B

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